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(54) Novel preceramic polymers derived from cyclic silazanes and halosilanes and a method for their preparation.

(57) This invention deals with novel polysilazane polymers, a method for their preparation, and the ceramic materials prepared thereby. The method comprises reacting a halogen-containing monosilane with a cyclic silazane or mixture of cyclic silazanes. An example of such a material is one which is prepared by the reaction of HSiCl₃ and $\{(CH_3)_2SiNH\}_x$.

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**NOVEL PRECERAMIC POLYMERS DERIVED FROM CYCLIC SILAZANES AND HALOSILANES AND A
METHOD FOR THEIR PREPARATION**

This invention deals with new and novel polysilazane polymers, a method for their preparation, their use to prepare ceramic materials and the ceramic materials prepared thereby. Said invention resides in the use of certain cyclic silazanes or mixtures of such cyclicsilazanes with halogen-containing monosilanes to give the unique polysilazane polymers.

5 Since about 1975, there has been a renewed effort in the synthesis of preceramic polymers owing to the fact that such polymers have handling properties which allow the formation of shapes and forms prior the ceramification. Thus, several different methods have been developed and disclosed for the preparation of polysilazane polymers that can be converted to silicon nitrogen-containing ceramics and other related materials.

10 The first reported methods was that of Verbeek in U.S. Patent No. 3,853,567, issued on December 10, 1974 in which methyltrichlorosilane was reacted with methylamine to form methyltris(methylamino)silane. This product could be heated to form a polymer at 520°C. The polymers could then be cured by moist air oxidation at 110°C. and then pyrolyzed to afford a low yielding Si-C-N-O ceramic. Similar materials and techniques were disclosed by Verbeek et. al. in U.S. Patent No. 3,892,583, issued July 1, 1975.

15 Some time later, Gaul, in U.S. Patent No. 4,312,970, issued January 26, 1982, disclosed the preparation of polysilazane polymers that were synthesized by reacting various alkyltrichlorosilanes with a disilazane, such as, $\{(CH_3)_3Si\}_2NH$. In this synthesis, $(CH_3)_3SiCl$ was eliminated as a by-product. These materials could by pyrolyzed at high temperatures to form Si-C-N containing ceramics.

20 In addition, Gaul, in U.S. Patent No. 4,404,153 issued July 20, 1982, obtained ceramics materials by pyrolysis of preceramic silazane polymers, which polymers were prepared by reacting chlorine-containing disilanes and disilazanes. These polymers were pyrolyzable to Si-C-N ceramics and prior to pyrolysis, the polymers were capable of being molded, i.e., one could form such shapes as fibers from such polymers.

25 In another, Cannady in U.S. Patent No. 4,543,344, issued September 24, 1985, prepared polymers by reacting $HSiCl_3$ and disilazanes. These materials were capable of being pyrolyzed to Si-C-N alloyed ceramics.

Cannady, later, in U.S. Patent No. 4,540,803, issued September 10, 1985 described a modification to Gaul's process to include the preparation of a polyhydridomethylsilazane polymer from trichlorosilane and hexamethyldisilazane.

30 Additional polymers have been developed and disclosed by Gaul in U.S. Patent No. 4,395,460, issued July 26, 1983; U.S. Patent No. 4,404,153, issued September 13, 1983; Haluska in U.S. Patent No. 4,482,689, issued November 13, 1984; Seyferth, et al. in U.S. Patent No. 4,397,828, issued August 9, 1983; and 4,482,669 issued November 13, 1984; Cannady in U.S. Patent No. 4,535,007, issued August 13, 1985; Bujalaski in U.S. Patent Application Serial No. 653,003, filed September 21, 1984; Baney, et al. in U.S. Patent Applications Serial Nos. 652,938, filed September 21, 1984 and 653,939, filed September 21, 1984.

35 What has been discovered are new and novel preceramic polymers, methods for their preparation, their use to prepare ceramic materials and the ceramic materials prepared using such preceramic polymers.

This invention relates to a method of preparing preceramic polymers, which method comprises contacting and reacting in an inert essentially anhydrous atmosphere, a halogen-containing monosilane or a mixture of halogen-containing monosilanes having the general formula

40 $R \overset{c}{\underset{|}{\overset{\circ}{S}}} X_{(4-c)}$
with a cyclic silazane or a mixture of cyclic silazanes selected from the group consisting of silazanes having the general formula (i) $(CH_3R''SiNH)_x$ and (ii) $(C_6H_5R''SiNH)_x$ at a temperature in the range of 0° to 260°C. while distilling by-produced volatile products, wherein R' and R'' are each independently selected from the group consisting of hydrogen, vinyl, phenyl and alkyl radicals containing 1 to 3 carbon atoms; c has a value of 1 or 2; and x has a value of 3 to 6 and X is a halogen atom.

This invention further comprises the method by which the product obtained by such a preparative method is further treated with ammonia to reduce the residual halide in such a polymer.

Also, this invention deals with the products produced by the preparative method for the preceramic polymers and the products produced by the ammonia treatment of such polymers.

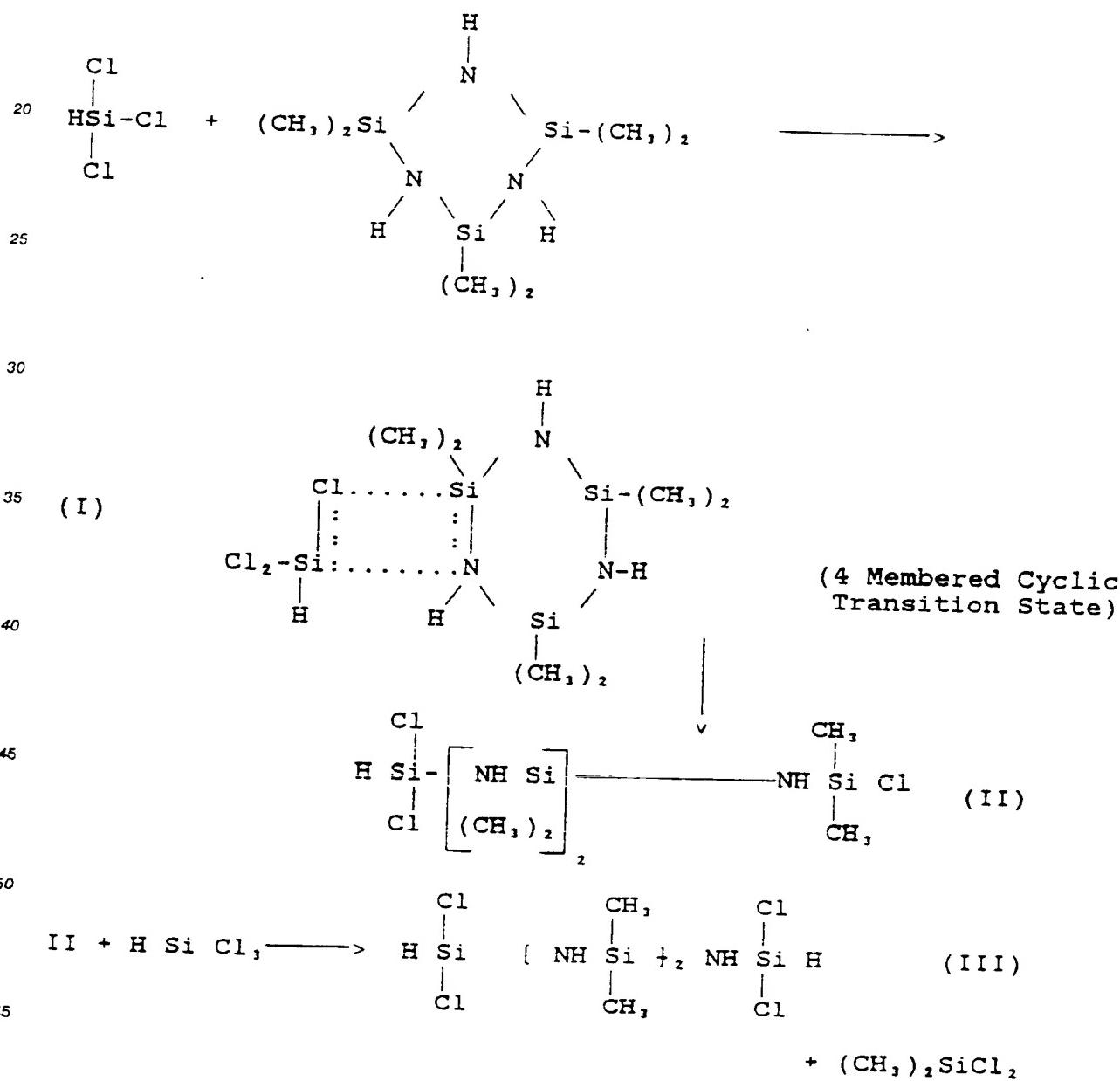
50 In addition, this invention deals with a method of forming a ceramic material, which method comprises pyrolyzing the preceramic polymer, or the ammonia treated preceramic polymer, at elevated temperatures, in a vacuum, or an inert atmosphere until the preceramic polymer or the ammonia treated preceramic polymer is converted to a ceramic material.

Finally this invention deals with the ceramic composition prepared by pyrolyzing the inventive compositions herein.

The preceramic polymers of this invention, including those not treated with ammonia, have improved flow characteristics over those materials of the prior art. It was discovered that the incorporation of significant amounts of dimethylsilazane, -SiMe₂NH-, substituted into the polymer rather than trimethylsilazane, Me₃SiNH-, improves the flow characteristics. It is believed by the inventor herein that such a benefit is due to enhanced polymer chain flexibility.

Thus, the preparation of the new polymers involve the reaction of $(\text{CH}_3\text{R}'\text{SiNH})_x$, or $(\text{C}_6\text{H}_5\text{R}'\text{SiNH})_x$, or a mixture of these cyclic silazanes, with halosilanes such as HSiCl_3 to eliminate $\text{RR}'\text{SiCl}_2$ wherein R and R' are individually CH_3 or C_6H_5 , as a by-product during the polymerization reaction to form the preceramic polymer. The remaining halide substitution on silicon can then be removed by reacting with gaseous ammonia.

It is theorized, but the inventor does not wish to be held to such a theory, that the following reactions take place, using HSiCl_3 and $\{\text{(CH}_3\text{)}_2\text{SiNH}\}_3$ as the reactants by way of example:



The residual chloride can then be essentially removed by treatment with gaseous ammonia, viz. $\text{III} + \text{NH}_3 \longrightarrow \text{Si NH}_2 + \text{NH}_4\text{Cl}$.

- Generally, the reaction of the silane and cyclic silazane is carried out in the presence of a solvent such as toluene. The solvent is not critical as any organic solvent that allows the compatibility of the reactants, without reacting with the silanes or the cyclic silazanes, can be used in this invention. Generally, since the initial reaction is exothermic, it is desirable to cool the reaction vessel as the reaction proceeds. Although it is not essential, it is preferred to add the silanes to the cyclic silazanes wherein the silazanes are cooled, such as by an ice water bath.

The amount of silane that can be reacted with the cyclic silazane is based on the stoichiometry of the total available halide in the silanes and the total available reactive nitrogen in the cyclic silazanes. Thus, preferred for this inventive method is a ratio of 1 equivalent of HSiCl_3 to 2.75 equivalents of $\{\text{(CH}_3)_2\text{SiNH}\}_x$. Other ratios of HSiCl_3 to $\{\text{(CH}_3)_2\text{SiNH}\}_x$ can be used that are higher or lower as long as the final product is soluble in organic solvents such as toluene, n-heptane, etc.

The reaction mass should be essentially dry as water tends to interfere with the desired results. After the silane has been added to the cyclic silazane and the initial exotherm has subsided, the cooling source is removed and the reaction is allowed to proceed at or near room temperature for a period of one to several hours depending on the silanes and cyclic silazanes used in the reaction. The reaction mass is then strip distilled to remove volatile by-products and to form the polymer. Preferred strip distillation temperature is in the range of 22°C. to 260°C. The polymer so-formed can then be filtered, stored or treated with gaseous ammonia to reduce the residual halide content. Further, it is appropriate to refilter the polymer after the gaseous ammonia treatment to remove the solid NH_4Cl that forms therein.

The polymers range from solids to liquids and are light to dark yellow in color. Monosilanes useful in this invention are those having the general formula $\text{R}_c\text{SiX}_{(4-c)}$ wherein R' is selected from the group consisting of hydrogen, vinyl, phenyl and alkyl radicals containing 1 to 3 carbon atoms and c has a value of 1 or 2 and X is halogen.

Thus, the monosilanes having the specific formulas HSiCl_3 , CH_3SiCl_3 , $\text{C}_6\text{H}_5\text{SiCl}_3$, $\text{CH}_2=\text{CHSiCl}_3$, $\text{CH}_3\text{CH}_2\text{SiCl}_3$ or $\text{CH}_3(\text{CH}_2)_2\text{SiCl}_3$ and double organic substituted silanes such as $(\text{CH}_3)_2\text{SiCl}_2$, $(\text{C}_2\text{H}_5)_2\text{SiCl}_2$ and $(\text{CH}_2=\text{CH})(\text{CH}_3)\text{SiCl}_2$ are examples of the silanes useful in this invention. Preferred in this invention are the silanes HSiCl_3 , CH_3SiCl_3 , $\text{CH}_2=\text{CHSiCl}_3$ and $\text{CH}_3(\text{CH}_2=\text{CH})\text{SiCl}_2$. Most preferred are the silanes HSiCl_3 and CH_3SiCl_3 .

Mixtures of the above silanes can also be used in this invention. For example, CH_3SiCl_3 and $\text{CH}_2=\text{CHSiCl}_3$ can be used to give a heterogenous polymer having vinyl functionality. The number of units of di-organo-substituted silicon atoms should not exceed the number of units of monoorgano-substituted silicon atoms. Even though silazane polymers can be formed from reactants wherein the di-organo-substituted units exceed the number of monoorgano-substituted units, it has been found that these polymers have much less desirable properties.

The cyclic silazanes useful in this invention are those having the general formulae (i) $(\text{CH}_3\text{R}'\text{SiNH})_x$ (ii) $(\text{C}_6\text{H}_5\text{R}'\text{SiNH})_x$ wherein R' is selected from the group consisting of hydrogen, vinyl, phenyl and alkyl radicals containing 1 to 3 carbon atoms and x has a value of 3, 4, 5 or 6. Preferred for this invention are those cyclic silazanes wherein x has a value of 3 or 4 and R' is methyl, vinyl, or phenyl. Most preferred are those cyclic silazanes wherein x has a value of 4 and R' is methyl.

Mixture of cyclic silazanes can be used. By "mixture", it is meant for purposes of this invention that the cyclics can be mixtures wherein x has the value of 3 and 4, or x has a value of 3, 4 and 5, etc. Generally, the cyclic silazanes are used in such mixtures wherein the cyclic tetramer predominates, that is, the cyclic tetramer is present in the mixture in more than fifty weight percent. "Mixtures" can also mean that, for example, cyclic tetramers having different substituents on silicon can be used. For example, $\{\text{(CH}_3)_2\text{SiNH}\}_4$ and $\{\text{CH}_3(\text{CH}_2=\text{CH})\text{SiNH}\}_4$ can be used together to give mixed polymers.

This invention also deals with a method of preparing ceramic materials, the method comprising heating a preceramic polymer which has been prepared by contacting and reacting in an inert, essentially anhydrous atmosphere, a halogen-containing monosilane or a mixture of halogen-containing monosilanes having the general formula

$\text{R}'\text{SiX}_{(4-c)}$ with a cyclic silazane or a mixture of cyclic silazanes selected from the group consisting of silazanes having the general formula (i) $(\text{CH}_3\text{R}'\text{SiNH})_x$ and (ii) $(\text{C}_6\text{H}_5\text{R}'\text{SiNH})_x$ at a temperature in the range of 0° to 260°C.

while distilling by-produced volatile products, wherein R' and R'' are each independently selected from the group consisting of hydrogen, vinyl, phenyl and alkyl radicals containing 1 to 3 carbon atoms; c has a value of 1 or 2; and x has a value of 3 to 6 and X is a halogen, atom in an inert atmosphere or vacuum to a temperature of at least 750°C. until said preceramic polymer is converted to a ceramic material.

5 Further, this invention deals with a method of preparing ceramic materials wherein a preceramic polymer is prepared by

(I) contacting and reacting in an inert, essentially anhydrous atmosphere, a halogen-containing monosilane or a mixture of halogen-containing monosilanes having the general formula R - SiX_(4-c)

10 with a cyclic silazane or a mixture of cyclic silazanes selected from the group consisting of silazanes having the general formula (i) (CH₃R'SiNH)_x and (ii) (C₆H₅R'SiNH)_x at a temperature in the range of 0° to 260°C. while distilling by-produced volatile products, wherein R' and R'' are each independently selected from the group consisting of hydrogen, vinyl, phenyl and alkyl radicals containing 1 to 3 carbon atoms; c has a value of 1 or 2; and x has a value of 3 to 6 and X is a halogen atom;

15 (II) treating the product from (I) with dry gaseous ammonia at a temperature in the range of 22°C. to 114°C. to remove essentially all residual halide in the product from (I);

(III) heating the product from (II) in an inert atmosphere or, vacuum or dry ammonia-containing atmosphere to a temperature of at least 750°C. until said preceramic polymer is converted to a ceramic material.

20 For purposes of this invention, "inert" means the use of gases such as N₂, Argon, Helium, Carbon Monoxide or Hydrogen.

Now, so that those skilled in the art can more fully understand and appreciate the invention, the following examples are presented. These examples should not be used to limit the scope of this invention as it is delineated in the claims.

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Example 1

Polyhydridomethylsilazane from {(CH₃)₂SiNH}₄.

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The preparation of this polymer was carried out by adding 94.7 grams (0.7 moles) of HSiCl₃ to an ice water cooled solution of 140.8 grams of {(CH₃)₂SiNH}₄ (0.48 moles) in 320 cc of dry reagent toluene. The entire addition was completed in 6 minutes and during this time the temperature rose from 6.5°C. to 21°C. The ice bath was removed and the reaction mixture was allowed to stand overnight (about 16 hours). The 35 reaction mixture was then strip-distilled to a pot temperature of 209°C. There was obtained 332.6 grams of distillate that contained 0.41 moles of (CH₃)₂SiCl₂ which accounted for 39 weight percent of the chloride in the starting silane. This polymer which was a light yellow colored material was dissolved in 200 cc of dry toluene and dry ammonia gas was bubbled through the solution at temperatures of 23° to 56° to 46°C. over a period of 45 minutes and then the polymer was heated to a final temperature of 114°C. and allowed 40 to cool to room temperature. After filtration, the polymer was isolated in a 65.4 grams yield by strip distillation to a 203°C. pot temperature. The polymer was very light colored and was a solid upon cooling.

The element analysis for the polymer showed 55.3 weight percent Si; 22.6 weight percent for carbon; 7.56 weight percent for hydrogen; 22.8 weight percent for nitrogen and nil chloride content, to give a calculated composition of Si_{2.0} C_{1.9} H_{7.5} N_{1.8}. The molecular weight of the polymer was obtained by gas 45 phase chromatography analysis with the column calibrated versus polystyrene corrected to a known silazane polymer from the comparative example herein. The weight average molecular weight was 5102.

The softening point of the polymer was determined by heating a sample at 5°C./minute rate in a DuPont 1090 thermal mechanical analyzer. A softening point of 50°C. was obtained for this sample.

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Example 2

A sample of the polymer prepared in Example 1 was subjected to pyrolysis without precuring. Thermogravimetric analysis of the uncured polymer afforded a 65 weight percent yield of ceramic with 55 pyrolysis to 1000°C. in helium. Weight loss began at about 140°C. and was finished at about 750°C.

A separate sample was pyrolyzed in 4" Lindberg Furnace under argon to 1200°C. over a period of 3 hours to afford a 62 weight percent yield of ceramic char.

X-ray diffraction showed the ceramic to be an amorphous material. The mass absorption coefficient for the ceramic was 34.1. The mass absorption coefficient that was calculated from the elemental analysis of the ceramic material was 37.7.

Analysis of the ceramic material derived at 1200°C. from the polymer showed the following results.

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	<u>Element</u>	<u>Weight Percent</u>
10	Si	57.6
	C	14.2
	N	26.2

Thus, the elemental composition of the ceramic was Si_{2.1} C_{1.2}N_{1.9}.

15 The ceramic material had a density of 2.443 grams/cc which was obtained by a Gradient Column Procedure.

Example 3

20 A polymer and then ceramic material was prepared by the prior art method of Cannady according to Example 1 of U.S. Patent No. 4,543,344 and compared to the materials of the instant invention. See Table I for the polymers and Table II for the ceramics.

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Table I
Comparison of the Polymers of the Instant Invention

<u>Polymer Example</u>	<u>Yield/%</u>	<u>Molecular Weight (\bar{M}_w)</u>	<u>T Ref. °C.</u>	<u>Composition</u>
1	27.8	5102	50	Si _{2.0} C _{1.9} N _{1.6} H _{7.5}
3	14.5	1760	35-40	Si _{1.6} C _{1.9} H _{7.9} N _{1.6}

Table II
Comparison of the Ceramics of the Instant Invention

<u>Ceramic Example</u>	<u>Yield/%</u>	<u>X-ray</u>	<u>MAC*</u>	<u>Density</u>	<u>g/cc</u>	<u>Ceramic Composition</u>
2	65	Amorphous	37.7	2.443	29.9 x 10 ⁶	Si _{2.1} C _{1.2} N _{1.9} O _{0.06}
3	57	Amorphous	N.D.	N.D.	N.D.	

* Mass absorption coefficient

** Youngs modulus

With regard to the polymer yield based on the weight of the two starting materials, the inventive polymer yield was essentially twice that obtained with the comparative polymer yield. In addition, the ceramic yield of the inventive polymer is also higher than the comparison polymer. The molecular weight of 5 the inventive polymer is about three times greater than that of the comparison polymer and thus the inventive polymer has better flow and processing characteristics.

It was easy to pull fibers from a hot liquid melt of the inventive polymers. From the above comparison of the properties of the two polymers, it appears that the inventive polymer has the advantages of higher yield, higher molecular weights and better potential control over the softening 10 points.

Claims

- 75 1. A method of preparing a preceramic polymer comprising contacting and reacting in an inert, essentially anhydrous atmosphere, a halogen-containing monosilane or a mixture of halogen-containing monosilanes having the general formula $R \in SiX_{(4-c)}$ with a cyclic silazane or a mixture of cyclic silazanes selected from silazanes having the general formula $(CH_3R^*SiNH)_x$ and $(C_6H_5R^*SiNH)_x$ at a temperature in the range of 0° to 260°C while distilling by-produced volatile products, wherein R' and R* are each independently selected from hydrogen, vinyl, phenyl and alkyl radicals containing 1 to 3 carbon atoms; c has a value of 1 or 2; and x has a value of 3 to 6 and X is a halogen atom.
2. A method as claimed in claim 1, wherein the halogen-containing monosilane is $HSiCl_3$ and the cyclic silazane is $\{(CH_3)_2SiNH\}_x$.
3. A method as claimed in claim 1, wherein the halogen-containing monosilane is $HSiCl_3$ and the cyclic silazanes are a mixture of $\{(CH_3)_2SiNH\}_4$ and $\{(CH_3)_2SiNH\}_3$.
- 25 4. A method as claimed in claim 1 wherein the halogen-containing monosilane is CH_3SiCl_3 and the cyclic silazane is $\{(CH_3)HSiNH\}_x$.
5. A method as claimed in claim 1 and 4, wherein x has a value of 4.
6. A method as claimed in claim 1 and 4, wherein x has a value of 3.
- 30 7. A method as claimed in claim 1 wherein the product is further treated with ammonia in an inert, essentially anhydrous atmosphere.
8. A preceramic polymer prepared by contacting and reacting in an inert, essentially anhydrous atmosphere a halogen-containing monosilane or a mixture of halogen-containing monosilanes having the general formula $R \in SiX_{(4-c)}$ with a cyclic silazane or a mixture of cyclic silazane selected from silazanes 35 having the general formula $(CH_3R^*SiNH)_x$ and $(C_6H_5R^*SiNH)_x$, wherein R' and R* are each independently selected from hydrogen, vinyl, phenyl and alkyl radicals containing 1 to 3 carbon atoms; c has a value of 1 or 2; and x has a value of 3 to 6 and X is a halogen atom.
9. A preceramic polymer as claimed in claim 8 which is prepared from a halogen-containing monosilane which is $HSiCl_3$ and the cyclic silazane which is $\{(CH_3)_2SiNH\}_x$.
- 40 10. A preceramic polymer as claimed in claim 8, which is prepared from a halogen-containing monosilane which is CH_3SiCl_3 and the cyclic silazane which is $\{(CH_3)HSiNH\}_x$.
11. A preceramic polymer as claimed in claim 9 or 10 wherein x has a value of 4.
12. A preceramic polymer as claimed in claim 9 or 10, wherein x has a value of 3.
- 45 13. A preceramic polymer obtained by further treating the product claimed in any one of claims 8 to 12 with ammonia in an inert essentially anhydrous atmosphere.
14. A method of preparing a ceramic material, the method comprising pyrolyzing in an inert atmosphere or in a vacuum, to a temperature of at least 750°C, a preceramic polymer as claimed in claim 13, until the preceramic polymer is ceramified, whereby a ceramic material is obtained.
- 50 15. A ceramic material obtained by treating the product of any of claims 1 to 6 with dry gaseous ammonia at a temperature in the range of from 22°C to 114°C to remove essentially all residual halide in the product and heating the resulting product in an inert atmosphere or, vacuum or dry ammonia-containing atmosphere to a temperature of at least 750°C until the product is ceramified.



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⑧ Novel preceramic polymers derived from cyclic silazanes and halosilanes and a method for their preparation.

⑨ This invention deals with novel polysilazane polymers, a method for their preparation, and the ceramic materials prepared thereby. The method comprises reacting a halogen-containing monosilane with a cyclic silazane or mixture of cyclic silazanes. An example of such a material is one which is prepared by the reaction of HSiCl₃ and {(CH₃)₂SiNH}_x.

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DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)						
X, P	PATENT ABSTRACTS OF JAPAN, vol. 12, no. 50 (C-476)[2897], 16th February 1988; & JP-A-62 199 623 (TOSHIBA SILICONE CO. LTD) 03-09-1987 * Abstract * ---	1,2,4,6 -10,12- 15	C 08 G 77/62 C 04 B 35/00 C 04 B 35/56						
A, D	US-A-4 312 970 (GAUL, Jr.) * Claims * ---	1-15							
A	EP-A-0 175 382 (DOW CORNING CORP.) * Claims 1,3 * & US-A-4 668 642 (Cat. D) -----	1-15							
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)						
			C 08 G C 04 B C 08 L						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>21-12-1989</td> <td>HOLLENDER C.J.F.</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	21-12-1989	HOLLENDER C.J.F.
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CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document							